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⑰ Applicant: **E.I. DU PONT DE NEMOURS AND  
COMPANY**  
1007 Market Street  
Wilmington Delaware 19898(US)

⑱ Inventor: **Frances, Arnold**  
1400 Arron Circle  
Wilmington Delaware 19803(US)

⑲ Representative: **Abitz, Walter, Dr.-Ing. et al**  
**Abitz, Morf, Gritschneider, Freiherr von**  
Wittgenstein Postfach 86 01 09  
D-8000 München 86(DE)

⑳ Masterbatch with fiber and liquid elastomer.

㉑ A particulate elastomeric composition is disclosed for use as a masterbatch material comprising aramid pulp, reinforcing fiber, and liquid elastomer. A process for making such composition is also disclosed.

**EP 0 272 459 A2**

## Masterbatch With Fiber and Liquid Elastomer

### Field of the Invention

This invention relates to a particulate elastomeric composition suitable for use as a masterbatch material to facilitate the blending of aramid pulp into elastomers. The invention also relates to a process for preparing the particulate elastomeric composition.

Reinforcement of elastomers with fibers or fibrous materials is well known. Such fibers or fibrous materials increase the modulus of the elastomer containing them and thus increase the resistance of the elastomer to stretch. Uniform blending of fibers and fibrous materials into elastomers can be difficult, especially when relatively large quantities, i.e. >5%, of the fiber or fibrous material are to be blended into the elastomer. This problem is particularly troublesome in the case of high strength, high modulus aramid fibers and pulp because the fibers and pulp are so strong that they are not broken in the mixing operation but rather tend to "ball-up" with consequent nonuniform dispersion throughout the elastomer.

British Patent 2,147,589 published May 15, 1985 discloses a method for dispersing aramid fibers into rubbery polymer solutions to make fiber-reinforced compositions.

United States Patent 4,514,541 issued April 30, 1985 on the application of the same inventor as herein, discloses an elastomeric composition for masterbatch use wherein the elastomeric material of the composition is utilized as a solution with a solvent which must be evaporated and recovered.

United States Patent 3,697,364 issued October 10, 1972 and United States Patent 3,836,412 issued September 17, 1974 on the applications of K. Boustany et al. disclose elastomeric compositions reinforced by cellulosic fibers wherein the fibers are treated before dispersion in the elastomer by being mixed with fillers or solvents or latices to be coagulated to solid elastomers. The compositions also comprise bonding agents for strong fiber-to-elastomer adhesion.

German Patent Application OLS 3,221,266 published December 8, 1983 on behalf of G. Bauer discloses sealing compositions which comprise elastomers and aramid fibers wherein the fibers are treated, before dispersion in the elastomer, by a coating of an opposite electrical charge, namely, for example, silicic acid. There is no masterbatch element to the dispersing process.

United States Patent 4,263,184 issued April 21, 1981 on the application of T. Leo et al. discloses a fibrous masterbatch composition for dispersion into elastomers wherein the masterbatch comprises fibers and a coagulated latex of elastomer or polymer.

United States Patent 3,998,778 issued December 21, 1976 on the application of G. Berg et al. discloses a filler masterbatch composition which is fiber-free and made by combining an emulsion of filler-containing elastomer solution with an aqueous alkali silicate solution to coagulate the elastomers.

Japanese Patent Laid-Open Publication 100,836/81 published August 13, 1981 discloses preparation of masterbatch blending compositions comprising NBR, carbon black, and aramid fiber. The NBR is solid and carboxylated. The carboxylation is used to increase adhesion to the aramid fiber.

United States Patent 3,931,094 issued January 6, 1976 on the application of L. Segel et al. discloses a composition of thermoplastic resin, filler, and fibrous dispersing aid wherein all of the filler and the fibrous dispersing aid are combined with all of the thermoplastic resin to yield a final filled product. There is no masterbatch element to the compounding process.

It is known to coat fibrous materials with elastomeric latices followed by coagulation of the latices to provide a mixture of fibrous material and elastomer useful in assisting the dispersion of the fibrous material into the same or another elastomer. Such elastomer-coated fibrous materials are generally in the form of a solid mass of fibers and elastomer which must be cut for further processing. This procedure has not been described using aramid pulp. Disadvantages of the procedure are that only elastomers available in latex form can be used and that use of such latices requires the removal of water from the final dispersion.

### Brief Description Of The Invention

This invention provides a particulate elastomeric composition which is suitable for use as a masterbatch material in compounding elastomeric products. The masterbatch material of the invention includes aramid pulp, reinforcing filler, and a liquid elastomer. The liquid elastomer is used without organic solvents and the masterbatch material, nevertheless, does not evidence the liquid nature of the elastomer.

The masterbatch material of this invention comprises 5 to 65 weight parts of aramid pulp, 10 to 65

weight parts of reinforcing filler, and 5 to 75 weight parts of the liquid elastomer. The masterbatch material is made by thoroughly mixing the aramid pulp and the reinforcing filler and then combining the pulp and filler with the liquid elastomer. The aramid pulp is preferably poly(p-phenylene terephthalamide) having lengths from 0.1 to 8 mm with an average length of about 1 to 3 mm and perhaps slightly larger; and the reinforcing filler is preferably carbon black or silica. The fiber length-to-diameter ratio is at least 10 and may be as much as 1000 or more. The liquid elastomer is preferably polybutadiene or co-polymers of butadiene and acrylonitrile with a viscosity of 20,000-70,000 centipoises at a shear rate ( $\text{sec}^{-1}$ ) of about 2 to 3 and at 25°C.

The particulate elastomeric composition of this invention is made using liquid elastomer with no solvents as an aid to preparation of the composition. Because the elastomer is liquid, there is no need to use solvents and, therefore, there is no need to remove solvent from the composition, once prepared. The liquid nature of the elastomer permits complete wetting by the elastomer of pulp particles in the composition and the small amounts of the liquid elastomer in the composition cause the composition to have a dry appearance. This invention provides for a dry, particulate, elastomer composition useful as a masterbatch material for compounding elastomers but without the disadvantages of using, evaporating, and recovering solvents from the composition.

#### Detailed Description Of The Invention

By aramid pulp is meant a synthetic pulp made by mechanical shattering of fibers derived from high strength, high modulus aromatic polyamide fibers such as those described in United States Patents 3,869,429 and 3,869,430. Particularly preferred is aramid pulp derived from poly(p-phenylene terephthalamide) fibers. Aramid pulp is preferably made using pulp refining methods which are used in the paper industry, for example, disc refining. The aramid fibers are shattered both transversely and longitudinally to provide fibers having a length of 0.1 to 8 mm, depending on the degree of refinement. Attached to these fibers are fine fibrils which have a diameter as small as 0.1  $\mu\text{m}$  as compared to a diameter of about 12  $\mu\text{m}$  for the main (trunk) part of the fiber. The aramid pulp has the appearance of hairy fibers. Aramid pulp has a Canadian Standard Freeness of 300-650  $\text{cm}^3$  and a Clark Classification (% on 14 mesh screen) of 5-45%. Preferred for use in the present invention is aramid pulp having a length in the range of 0.5-4 mm and an average length of about 2 mm, a Canadian Standard Freeness of 300-450  $\text{cm}^3$  and a Clark Classification of 5-15%. Less preferred, but still useful is longer pulp having a length of 0.1 to 8 mm and an average length of from about 1 to 5 mm having a Canadian Standard Freeness of 525-650  $\text{cm}^3$  and a Clark Classification of 20-45%.

High strength, high modulus aromatic polyamide fibers are derived from aromatic polyamides whose chain extending bonds are either coaxial or parallel and oppositely directed. Such fibers are described in United States Patents 3,869,429 and 3,869,430 and may be prepared by the spinning process described in United States Patent 3,767,756.

The fillers useful in the present invention are the usual reinforcing fillers useful for compounding into elastomers, for example, carbon blacks and structured silica.

Liquid elastomers useful in practice of this invention include elastomers of low enough molecular weight and few enough crosslinks that the elastomer material, itself, without solvents, diluents, or other additives exhibits a viscosity of 1 to  $10^6$  centipoises as determined at shear rates of 2 to 3  $\text{sec}^{-1}$  and at the temperature of mixing. Liquid elastomers have not been used in masterbatch compositions prior to the present invention. One essential criterion for use of a liquid elastomer is that the elastomer must have a viscosity which is appropriate for mixing with the filler, fiber, and other components at the temperature at which the mixing is conducted. Mixing of the components is generally conducted at about 20-50°C and less than 100°C. It has been concluded that the liquid elastomer can be combined with the other components so long as the viscosity of the elastomer is less than about  $10^6$  centipoises. The lower limit is a practical limitation of little critical importance because the components can be easily combined when the elastomer has a low viscosity.

Specifically preferred for use in this invention are liquid elastomers of polybutadiene and copolymers of butadiene and acrylonitrile. Other liquid elastomers which can be used are elastomers of polymers and copolymers of alkenes having less than five carbon atoms such as vinylidene fluoride and hexafluoropropylene and styrenes such as styrene and vinylstyrene, and butadienes and acrylonitriles.

However, any liquid elastomer within the specified viscosity and compatibility limits can be used in practice of this invention. When the composition of the invention is used as a masterbatch material, the liquid elastomer must, of course, be chosen to be compatible and compoundable with the elastomer of the

final compound and compatible with the physical and chemical requirements of the first product.

Liquid elastomers which are particularly useful in practice of this invention are:

- "Hycar" 1312 LV - A copolymer of 74 weight percent butadiene and 26 weight percent acrylonitrile with a molecular weight of about 1000, and a viscosity of about 60,000 to 70,000 centipoises at a shear rate of 2 to 3 sec<sup>-1</sup> at 25°C. This product is sold by B.F. Goodrich.
- "Ricon" 150 - 1,2-vinylpolybutadiene with 70 weight percent vinyl and about 8 weight percent cis- and about 22 weight percent trans-butadiene, a molecular weight of about 1800-2400, and a viscosity of about 30,000 to 50,000 centipoises at a shear rate of 2 to 3 sec<sup>-1</sup> at 25°C. This product is sold by Colorado Chemical Specialties, Inc.
- Neoprene FB - A polymer of 2-chloro-1,3-butadiene with a viscosity of about 50,000-150,000 centipoises at 50°C. This product is sold by E. I. du Pont de Nemours and Company.
- "Viton" LM - A polymer of vinylidene fluoride and hexafluoropropylene with a Brookfield viscosity of about 2000 centipoises at 100°C. This product is sold by E. I. du Pont de Nemours and Company.
- "Ricon" 100 - 1,2-vinylstyrene butadiene rubber with a molecular weight of about 2400 and a viscosity of about 400,000 centipoises at a shear rate of 2 to 3 sec<sup>-1</sup> at 25°C.
- "Ricon" 181 and 184 - styrene butadiene rubbers with a molecular weight of about 3000 for "Ricon" 181 and about 6500 for "Ricon" 184 and viscosities of about 8000 to 20,000 centipoises at a shear rate of 2 to 3 sec<sup>-1</sup> at 25°C.
- "Hycar" 1312 - A copolymer of 72 weight percent butadiene and 28 weight percent acrylonitrile with a viscosity of about 120,000 to 140,000 centipoises at a shear rate of 2 to 3 sec<sup>-1</sup> at 25°C.

#### General Procedure For Preparing The Particulate Elastomeric Composition of the Invention

- A pulp, such as an aramid pulp as sold by E. I. du Pont de Nemours and Company under the trademark "Kevlar" and a typical reinforcing filler such as carbon black or silica are placed in a high speed mixer. The pulp/filler ratio can vary from about 1/6 to 4/1, depending on the requirements of the ultimate, reinforced elastomeric product. The mixer (Erich RV02 Model 22496 at 3225 rpm chopper blade speed and 71 rpm pan speed or Littleford Model #FM-310-D at 3600 rpm chopper speed and 155 rpm plow speed) is run for about two minutes to separate the pulp into individual fibers and blend the fibers with the filler.

- The mixer is then opened and liquid elastomer is added. The material is mixed at high speed for about 4 minutes, and the mixer turned off and opened. The resulting particles may be very fine and fibrous or larger and irregularly shaped (usually 0.2-2.5 cm). The particle size is primarily dependent upon the amount of liquid elastomer used. The less elastomer, the smaller the particle. The particular filler and filler amount also have some effect on particle size. For ease of dispersion, smaller sized particles are preferred.

The particles are now ready for use as a masterbatch for compounding in elastomer stock.

#### Tests

##### Dispersion in Elastomers

- To determine the effectiveness of the masterbatch material of this invention, particles of the material are compounded with a standard rubber stock using standard compounding techniques. The particles and rubber stock are mixed using a Banbury mixer, sheeted by a single pass in a roll mill, and cooled to room temperature and then mixed a second time in the Banbury and milled and sheeted again in a roll mill in which the rolls are operated at different circumferential speeds. An uncured sheet is formed. The sheet is press-cured at 1000-1500 psi (6,900-10,350 kPa) and 320°F (160°C) for 20 minutes into a 0.075 inch thick slab, about 6 inches square (15 x 15 x 0.19 cm). The standard rubber stock which is often used is a sulfur-curable, low viscosity hydrocarbon rubber identified as "Nordel" 1040 and sold by E. I. du Pont de Nemours and Company.

Physical properties are measured at room temperature. In all cases, at least 5 replicates per sample are run. Measurements are by the following methods:

Tear Strength: ASTM D-624-54 (using die C)

- Modulus (tensile strength): ASTM D-412-68 (using die C)

The tests are conducted at about 75°F and about 50% relative humidity with no sample conditioning. The tests are conducted and reported using non-SI units. For the tensile tests, a crosshead speed of 20 inches per minute is utilized. The moduli are calculated by determining tensile strengths at particular elongations.

In the following examples, masterbatch materials of the invention were prepared and evaluated, as described, generally, hereinbelow, and using the specific kinds and amounts of component ingredients as indicated in the tables.

To make the particulate elastomeric masterbatch material, in Eirich mixer was charged with reinforcing filler and an aramid pulp having a length of 0.1 to 8 mm, average length about 2 mm. (The pulp was poly(p-phenylene terephthalamide) sold under the trademark "Kevlar" by E. I. du Pont de Nemours & Co.). The mixer was closed and the dry solids were blended for about 2 minutes. The mixer was turned off and opened; and liquid elastomer was added. The mixer was, again, closed and the mixture was blended for about 4 minutes.

To evaluate the particulate elastomeric masterbatch material, it was compounded with an elastomer and the compounded elastomer was tested for physical qualities. Elastomer, masterbatch material, and cure system components were added to an OOC Banbury mixer. The mixer was run at 50 to 70 revolutions per minute for about 9 minutes during which time the temperature of the material was permitted to increase from about room temperature to less than about 300°F. The dry mixture was removed from the mixer and was sheeted in a single pass on a roll mill and allowed to cool to room temperature. The cooled, sheeted, mixture was placed again in the Banbury mixer along with cure system components and the mixer was run at 70 revolutions per minute for 2 minutes during which time the temperature of the materials was permitted to increase from about room temperature to less than about 220°F. The dry mixture was removed from the mixer and was milled on a roll mill until all ingredients were uniformly blended. The resulting, uniformly blended, sheet was slit, removed from the roll, cut to size, and cured for 20 minutes at 160°C (320°F) under pressure of 6900-10,350 kPa (1000-1500 psi). The cured slab was 15 x 15 x 0.19 cm (6 x 6 x 0.075 inch).

#### Example 1

In this example, the reinforcing filler was "Hi Sil" 233 and the liquid elastomer was "Hycar" 1312 LV. The several masterbatch compositions are indicated in Table 1-1, as parts by weight and by weight percentages.

"Hi Sil" 233 is a highly structured silica, particle size about 0.02  $\mu$ m in diameter. The product has a surface area of 140 m<sup>2</sup>/g and is sold by Pittsburgh Plate Glass.

**Table 1-1**

Sample	Liquid Elastomer		Filler		Pulp	
	Parts	%	Parts	%	Parts	%
1-1	100	20.0	200	40.0	200	40.0
1-2	25	5.9	200	47.1	200	47.1
1-3	50	11.1	200	44.4	200	44.4
1-4	200	33.3	200	33.3	200	33.3
1-5	400	50.0	200	25.0	200	25.0
1-6	600	60.0	200	20.0	200	20.0
1-7	100	32.3	10	3.2	200	64.5
1-8	100	31.2	20	6.2	200	62.5
1-9	100	28.6	50	14.3	200	57.1
1-10	100	25.0	100	25.0	200	50.0
1-11	100	14.3	400	57.1	200	28.6
1-12	100	11.1	600	66.7	200	22.2
1-13	100	32.3	200	64.5	10	3.2
1-14	100	31.2	200	62.5	20	6.3
1-15	100	28.6	200	57.1	50	14.3
1-16	100	25.0	200	50.0	100	25.0
1-17	100	14.3	200	28.6	400	57.1

The several masterbatch compositions were compounded with elastomer and other components as

described previously. For evaluation of this masterbatch composition, the masterbatch material, usually with additional filler, was compounded, in a first step, with a copolymer of butadiene and acrylonitrile sold under the trade designation "Hycar" VT-355 by B.F. Goodrich; and in a second step, with the following curing system components:

- 5 sulfur 2.0 phr  
 "Altax" 1.5 phr  
 MBT 1.0 phr  
 zinc oxide 5.0 phr  
 stearic acid 0.7 phr.

- 10 The indicated amounts of curing system components were used in parts per hundred parts of combined, liquid and solid, elastomer.

"Altax" is a benzothiazyl disulfide cure accelerator sold by R.T. Vanderbilt, Inc.

MBT is 2-mercaptobenzothiazole used as a cure accelerator.

- 15 Amounts of materials used in the first compounding step are indicated in Table 1-2. Amounts under columns headed by "MB" are amounts from masterbatch addition and amounts under columns headed by "Added" are amounts from separate addition of those individual ingredients to yield the desired composition. All pulp was added by means of the masterbatch materials.

**Table 1-2**

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		Elastomer (%)			Filler		Pulp
		<u>Solid</u>	<u>Liquid</u>				<u>MB</u>
<u>Sample</u>			<u>MB</u>	<u>Added</u>	<u>MB</u>	<u>Added</u>	
25	Control	95	0	5	0	40	10 (Added)
	1-1	95	5	0	10	30	10
	1-2	95	1.2	3.8	10	30	10
	1-3	95	2.5	2.5	10	30	10
	1-4	90	10	0	10	30	10
30	1-5	80	20	0	10	30	10
	1-6	70	30	0	10	30	10
	1-7	95	5	0	0.5	39.5	10
	1-8	95	5	0	1	39	10
	1-9	95	5	0	2.5	37.5	10
35	1-10	95	5	0	5	35	10
	1-11	95	5	0	20	20	10
	1-12	95	5	0	30	10	10
	1-13	70	30	0	60	0	3
	1-14	70	30	0	60	0	6
	1-15	80	20	0	40	0	10
40	1-16	90	10	0	20	20	10
	1-17	97.5	2.5	0	5	35	10

- 45 The Control was made by adding the indicated amounts of liquid elastomer, filler, and pulp separately, as individual ingredients in the first compounding step.

The compositions of Table 1-2 were, then, compounded in the second compounding step and were evaluated for physical properties. The results of those evaluations are in Table 1-3.

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Table 1-3

Sample	% Elong.	Tensile psi	Tear Str.	Modulus psi at 20°C			
				10%	20%	50%	100%
Control	120	1823	276	319	808	1664	1808
1-1	121	1834	319	864	1371	1834	
1-2	144	1888	365	579	1124	1767	1895
1-3	162	1809	368	310	665	1545	1795
1-4	190	1751	365	659	1077	1659	1736
1-5	87	1874	382	1105	1530	1868	1843
1-6	34	1994	308	1436	1741	1994*	
1-7	134	1696	367	245	434	1511	1683
1-8	168	1688	312	301	481	1031	1511
1-9	186	1533	323	362	596	1241	1546
1-10	118	1557	323	384	632	1174	1486
1-11	128	1779	332	437	768	1374	1689
1-12	142	1877	338	288	530	1593	1886
1-13	470	1502	262	309	712	1101	1129
1-14	206	1418	314	271	694	1339	1329
1-15	132	1694	354	395	635	1127	1470
1-16	149	1869	381	556	1063	1614	1677
1-17	154	1499	364	289	595	1285	1501

\*Indicates the modulus at break

As an analysis of the test results, Table 1-4 is provided, below, to show moduli for compositions, based on 100 weight parts of solid and liquid elastomer, wherein the masterbatch contains 5 weight parts liquid elastomer, 10 weight parts pulp, and varying amounts of filler.

Table 1-4

Sample	Filler in MB (wt)		Modulus		
	Parts	%	10%	20%	50%
Control	0	0	319	808	1664
1-7	0.5	3.2	245	434	1511
1-8	1	6.3	301	481	1031
1-9	2.5	14.3	362	596	1241
1-10	5	25	384	632	1174
1-11	10	40	864	1371	1834
1-11	20	57.1	437	768	1374
1-12	30	66.7	288	530	1593

Table 1-4 shows that the effect of the concentration of filler in the masterbatch is more pronounced at low stretch modulus tests; and that there is improvement in using a masterbatch over the Control when the masterbatch has from about 10 to about 65 weight percent filler. This table indicates that the masterbatch can, preferably, have from about 25 to 55 weight percent filler.

Further analysis of the test results are shown in Table 1-5 wherein moduli are tabulated for compositions, based on 100 weight parts of solid and liquid elastomer and the masterbatch contains 10 weight parts filler, 10 weight parts pulp, and varying amounts of liquid elastomer.

Table 1-5

Sample	Liq. elas. in MB (wt)		Modulus		
	Parts	%	10%	20%	50%
Control	0	0	319	808	1664
1-2	1.2	5.9	579	1124	1767
1-3	2.5	11.1	310	665	1545
1-1	5	20	864	1371	1834
1-4	10	33.3	659	1077	1659
1-5	20	50	1105	1530	1868
1-6	30	60	1436	1741	-

Table 1-5 shows that moduli are improved over the entire range tested when ingredients are compounded by means of a liquid elastomer masterbatch rather than by introduction of separate, uncombined, ingredients. The range tested extends to masterbatches having from about 5 to 60 weight percent liquid elastomer.

Finally, analysis of the test results are shown in Table 1-6 wherein moduli are tabulated for compositions formulated to have varying amounts of pulp. Because all of the pulp is added by means of the masterbatch, this analysis could not be made with constant amounts of liquid elastomer and filler.

Table 1-6

Sample	Pulp in MB (wt)		Modulus		
	Parts	%	10%	20%	50%
Control	0	0	319	808	1664
1-13	3	3.2	309	712	1101
1-14	6	6.3	271	694	1339
1-15	10	14.3	395	635	1127
1-16	10	25	556	1063	1614
1-1	10	40	864	1371	1834
1-10	10	50	384	632	1174
1-17	10	57.1	289	595	1285
1-8	10	62.5	301	481	1031
1-7	10	64.5	245	434	1511

Table 1-6 shows that the effect of the presence of pulp is more pronounced at low stretch modulus tests; and that there is improvement in using a masterbatch over the control when the masterbatch has from about 5 to about 55 weight percent pulp. This table indicates that the masterbatch can, preferably, have from about 10 to 50 weight percent pulp.

Example 2

In this example, the reinforcing filler was "Hi Sil" 233 and the liquid elastomer was "Ricon" 150. The several masterbatch compositions are indicated in Table 2-1, as parts by weight and by weight percentages.



Table 2-1

Sample	Liquid Elastomer		Filler		Pulp	
	Parts	%	Parts	%	Parts	%
2-1	100	20.0	200	40.0	200	40.0
2-2	25	5.9	200	47.1	200	47.1
2-3	50	11.1	200	44.4	200	44.4
2-4	200	33.3	200	33.3	200	33.3
2-5	400	50.0	200	25.0	200	25.0
2-6	600	60.0	200	20.0	200	20.0
2-7	100	32.3	10	3.2	200	64.5
2-8	100	31.2	20	6.2	200	62.5
2-9	100	28.6	50	14.3	200	57.1
2-10	100	25.0	100	25.0	200	50.0
2-11	100	14.3	400	57.1	200	28.6
2-12	100	11.1	600	66.7	200	22.2
2-13	100	32.3	200	64.5	10	3.2
2-14	100	31.2	200	62.5	20	6.3
2-15	100	28.6	200	57.1	50	14.3
2-16	100	25.0	200	50.0	100	25.0
2-17	100	14.3	200	28.6	400	57.1

The several masterbatch compositions were compounded with elastomer and other components, as described previously. For evaluation of this masterbatch composition, the masterbatch material, usually with additional filler, was compounded, in a first step, with a hydrocarbon rubber sold by E. I. du Pont de Nemours and Company under the trademark designation "Nordel" 1040; and, in a second step, with the following curing system components:

"Varox" DBPH 50 4 phr

TAC 2 phr

"Maglite D" 15 phr

The indicated amounts of curing system components were used in parts per hundred parts of combined, liquid and solid, elastomer.

"Varox" DBPH 50 is 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexane used as a vulcanizing, cross-linking agent and sold by R.T. Vanderbilt.

TAC is triallylcyanurate used as a cure accelerator.

"Maglite D" is a magnesium oxide vulcanizer, activator, and acid acceptor sold by the C.P. Hall Co., Merck Chemical Division.

Amounts of materials used in the first compounding step are indicated in Table 2-2. Amounts under columns headed by "MB" are amounts from masterbatch addition and amounts under columns headed by "Added" are amounts from separate addition of those individual ingredients to yield the desired composition. All pulp was added by means of the masterbatch materials.

Table 2-2

Sample	Elastomer (%)			Filler		Pulp
	Solid	Liquid		MB	Added	MB
Control	95	0	5	0	40	10(Added)
2-1	95	5	0	10	30	10
2-2	95	1.2	3.8	10	30	10
2-3	95	2.5	2.5	10	30	10
2-4	90	10	0	10	30	10
2-5	80	20	0	10	30	10
2-6	70	30	0	10	30	10
2-7	95	5	0	0.5	39.5	10
2-8	95	5	0	1	39	10
2-9	95	5	0	2.5	37.5	10
2-10	95	5	0	5	35	10
2-11	95	5	0	20	20	10
2-12	95	5	0	30	10	10
2-13	70	30	0	60	0	3
2-14	70	30	0	60	0	6
2-15	80	20	0	40	0	10
2-16	90	10	0	20	20	10
2-17	97.5	2.5	0	5	35	10

The Control was made by adding the indicated amounts of liquid elastomer, filler, and pulp separately, as individual ingredients in the first compounding step.

The compositions of Table 2-2 were, then, compounded in the second compounding step and were evaluated for physical properties. The results of those evaluations are in Table 2-3.

Table 2-3

Sample	% Elong.	Tensile psi	Tear Str.	Modulus psi at 20°C			
				10%	20%	50%	100%
Control	78	1224	282	524	818	1158	1172
2-1	23	1326	287	1016	1211	1326*	
2-2	13	1307	279	920	1307*		
2-3	69	1162	262	854	1072	1154	-
2-4	13	1356	253	1039	1392	1356*	
2-5	14	1763	245	1424	1763*		
2-6	7	1687	223	1687*			
2-7	53	1251	-	1243	1264	1170	-
2-8	73	1231	-	1006	1125	1159	-
2-9	136	1123	-	563	990	1125	1129
2-10	141	1121	-	663	1096	1108	1070
2-11	105	1224	-	701	1129	1202	-
2-12	88	1237	-	514	897	1212	1187
2-13	11	1982	238	1804	1982*		
2-14	4	1837	210	1837*			
2-15	8	1509	231	1448	1509*		
2-16	11	1542	220	1536	1542*		
2-17	194	959	274	687	843	902	-

\*Indicates modulus at break

As an analysis of the test results, Table 2-4 is provided, below, to show moduli for compositions, based on 100 weight parts of solid and liquid elastomer, wherein the masterbatch contains 5 weight parts liquid elastomer, 10 weight parts pulp, and varying amounts of filler.

Table 2-4

<u>Sample</u>	<u>Filler in MB (wt)</u>		<u>Modulus</u>	
	<u>Parts</u>	<u>%</u>	<u>10%</u>	<u>20%</u>
Control	0	0	524	818
2-7	0.5	3.2	1243	1264
2-8	1	6.3	1006	1125
2-9	2.5	14.3	563	990
2-10	5	25	663	1096
2-1	10	40	1016	1211
2-11	20	57.1	701	1129
2-12	30	66.7	514	897

Table 2-4 shows that the effect of the concentration of filler in the masterbatch is apparent at high stretch moduli as well as at low stretch moduli; and that there is improvement in using a masterbatch over the control when the masterbatch has from less than 3 weight percent up to at least 65 weight percent filler.

Further analysis of the test results from Example 2 are shown in Table 2-5 wherein moduli are tabulated for compositions, based on 100 weight parts of solid and liquid elastomer and the masterbatch contains 10 weight parts filler, 10 weight parts pulp, and varying amounts of liquid elastomer.

Table 2-5

<u>Sample</u>	<u>Liq. elas. in MB (wt)</u>		<u>Modulus</u>	
	<u>Parts</u>	<u>%</u>	<u>10%</u>	<u>20%</u>
Control	0	0	524	818
2-2	1.2	5.9	920	1307*
2-3	2.5	11.1	854	1072
2-1	5	20	1016	1211
2-4	10	33.3	1039	1392
2-5	20	50	1424	1763*
2-6	30	60	1687*	--

\* Indicates the modulus at break.

Table 2-5 shows that moduli are improved over the entire range tested when ingredients are compounded by means of a liquid elastomer masterbatch rather than by introduction of separate, uncombined, ingredients. The range tested extends to masterbatches having from less than 6 weight percent up to at least 60 weight percent liquid elastomer.

Finally, analysis of the test results are shown in Table 2-6 wherein moduli are tabulated for compositions formulated to have varying amounts of pulp. Because all of the pulp is added by means of the masterbatch, this analysis could not be made with constant amounts of liquid elastomer and filler.

Table 2-6

Sample	Pulp in MB (wt)		Modulus	
	Parts	%	10%	20%
Control	0	0	524	818
2-13	3	3.2	1804	1982*
2-14	6	6.3	1837*	--
2-15	10	14.3	1448	1509*
2-16	10	25	1536	1542*
2-1	10	40	1016	1211
2-10	10	50	663	1096
2-17	10	57.1	687	843
2-8	10	62.5	1006	1125
2-7	10	64.5	1243	1264

\* Indicates the modulus at break.

Table 2-6 shows that moduli are improved over the entire range tested, from less than 3 weight percent to more than 65 weight percent pulp, when ingredients are compounded by means of a liquid elastomer masterbatch rather than by introduction of separate, uncombined, ingredients. The table also shows that there is more pronounced improvement when the masterbatch has from less than about 3 weight percent up to about 50 weight percent pulp.

#### Claims

1. A particulate elastomeric composition for use as a masterbatch material comprising 5 to 65 weight parts of aramid pulp, 10 to 65 weight parts of reinforcing filler, and 5 to 75 weight parts of liquid elastomer.
2. The composition of Claim 1 wherein the aramid pulp is poly(p-phenylene terephthalamide) pulp.
3. The composition of Claim 2 wherein the pulp has a length of 0.1 to 8 mm.
4. The composition of Claim 1 wherein the reinforcing filler is selected from the group consisting of carbon black and silica.
5. The composition of Claim 1 wherein the liquid elastomer is selected from the group consisting of polymers and copolymers of alkylenes having less than five carbon atoms, styrenes, butadienes, and acrylonitriles.
6. The composition of Claim 1 wherein the viscosity of the liquid elastomer is less than  $10^6$  centipoises at a shear rate of 2-3 sec<sup>-1</sup> at 50°C.
7. A process for making a particulate elastomeric composition comprising thoroughly mixing 5 to 65 weight parts of aramid pulp with 10 to 65 weight parts of reinforcing filler and then combining the mixed pulp and filler with 5 to 75 weight parts of liquid elastomer.
8. The process of Claim 7 wherein the aramid pulp is poly(p-phenylene terephthalamide) pulp.
9. The process of Claim 8 wherein the pulp has a length of 0.1 to 8 mm.
10. The process of Claim 7 wherein the reinforcing filler is selected from the group consisting of carbon black and silica.
11. The process of Claim 7 wherein the liquid elastomer is selected from the group consisting of polymers and copolymers of alkylenes having less than five carbon atoms, styrenes, butadienes, and acrylonitriles.
12. The process of Claim 7 wherein the viscosity of the liquid elastomer is less than  $10^6$  centipoises at a shear rate of 2-3 sec<sup>-1</sup> at 50°C.

⑫

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⑦① Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**  
**1007 Market Street**  
**Wilmington Delaware 19898 (US)**

⑦② Inventor: **Frances, Arnold**  
**1400 Arron Circle**  
**Wilmington Delaware 19803 (US)**

⑦④ Representative: **Abitz, Walter, Dr.-Ing. et al**  
**Abitz, Morf, Gritschneider, Freiherr von Wittgenstein**  
**Postfach 86 01 09**  
**D-8000 München 86 (DE)**

⑤④ Masterbatch with fiber and liquid elastomer.

⑤⑦ A particulate elastomeric composition is disclosed for use as a masterbatch material comprising aramid pulp, reinforcing fiber, and liquid elastomer. A process for making such composition is also disclosed.

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## EUROPEAN SEARCH REPORT

Application Number

EP 87 11 7145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,Y	US-A-4 514 541 (A. FRANCES) * Claim 1; column 3, lines 20-23 * ---	1-12	C 08 J 3/22 C 08 L 21/00 //
Y	US-A-4 564 670 (J.E. KEARNAN) * Claim 1; column 2, lines 11-16 * ---	1-12	(C 08 L 21/00 C 08 L 77:10 )
D,A	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 178 (C-78)[850], 14th November 1981; & JP-A-56 100 836 (NIPPON OIL SEAL KOGYO K.K.) 13-08-1981 * Abstract * ---		
A	DATABASE WPIL, no. 81-18621D, Derwent Publications Ltd, London, GB; & JP-A-56 005 879 (FURUKAWA ELECTRIC CO.) 21-01-1981 * Abstract * ---		
A	US-A-4 098 715 (T. MASUKO et al.) * Claim 1 * ---		
D,A	GB-A-2 147 589 (POLYSAR FINANCIAL SERVICES) * Claim 1 * -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 J C 08 L
Place of search THE HAGUE		Date of completion of the search 03-03-1988	Examiner VAN HUMBEECK F.W.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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